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Remarks:

The references to the drawing (Fig. 1) are deemed to be deleted (Rule 43 EPC).

(54) **Reactor blends of small amounts of syndiotactic polypropylene in isotactic polypropylene**

(57) Polymer blends of isotactic polypropylene and syndiotactic polypropylene enhance the processability in film applications. Up to a level of 4% by weight of syndiotactic polypropylene will increase the molecular weight distribution. Up to a level of 13.9% by weight of syndiotactic polypropylene the clarity or haze of biaxially oriented film is improved. Within a range from about 2.34% by weight of syndiotactic polypropylene to about 13.9% by weight the melt flow is higher than that for either a syndiotactic homopolymer or an isotactic homopolymer. Within a range from about 2% by weight of syndiotactic polypropylene to about 13.9% by weight the level of xylene solubles is higher than that for either a syndiotactic homopolymer or an isotactic homopolymer. If appropriate catalysts are selected, a reactor blend may be produced of the desired mixture.

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DETAILED DESCRIPTION OF THE INVENTION

Olefins, especially propylene, may be polymerized to form polyolefins in amorphous (atactic) or crystalline forms. Examples of crystalline forms are isotactic and syndiotactic.

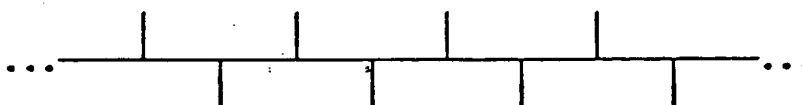
Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



The methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer, e.g., the methyl groups are all above or below the plane.

Another way of describing the structure is through the use of NMR. Bovey's NMR nomenclature for an isotactic pentad is ...mmmm... with each "m" representing a "meso" dyad or successive methyl groups on the same side in the plane. As known in the art, any deviation or inversion in the structure of the chain lowers the degree of isotacticity and crystallinity of the polymer.

A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:



The methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer.

In NMR nomenclature, this pentad is described asrrrr... in which each "r" represents a "racemic" dyad, i.e., successive methyl groups on alternate side of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer. Syndiotactic polymers are crystalline and like the isotactic polymers are insoluble in xylene. This crystallinity distinguishes both syndiotactic and isotactic polymers from atactic polymer that is soluble in xylene.

A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the crystalline form. One indication of the amount of atactic polymer is amount of polymer soluble in hot xylene (xylene solubles).

A multi-catalyst system for the polymerization of propylene in which separate polymerizations with a homogeneous catalyst and with a heterogeneous catalyst are possible. Preferably, the multi-catalyst system is useful in the polymerization of olefins, more preferably, α -olefins, and, most preferably, propylene. This catalyst system is disclosed in U.S. Serial No. 776,498 filed October 11, 1991, hereby incorporated by reference.

A multi-catalyst system of the present invention is obtained by mixing the components of at least one metallocene catalyst and at least one conventional supported Ziegler-Natta catalyst. Generally, the components of a metallocene catalyst are a metallocene compound and an ionizing agent. Generally, the components of a conventional supported Ziegler-Natta catalyst are an aluminum alkyl and a transition metal compound with, optionally, an electron donor.

Any of the conventional heterogeneous Ziegler-Natta transition metal compound catalyst components for producing isotactic polyolefins can be used in the present invention. The compound is preferably of the general formula MR^+_x where M is the metal, R_+ is a halogen or a hydrocarboxyl and x is the valence of the metal. Preferably, M is a Group IVB, VB or VIB metal, more preferably a Group IVB, and most preferably titanium. Preferably, R^+ is chlorine, bromine, an alkoxy or a phenoxy, more preferably chlorine or ethoxy and most preferably, chlorine. Illustrative examples of the transition metal compound catalyst components are $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ and $Ti(OC_{12}H_{25})Cl_3$. Mixtures of the transition metal compounds may be used. No restriction on the number of transition metal compounds is made as long as at least one transition metal compound is present.

The transition metal compound is supported on an inert solid which is chemically unreactive with any of the components of the heterogeneous or homogeneous catalyst. The support is preferably a magnesium compound. Examples of the magnesium compounds which are to be used to provide a support source for the catalyst component are magnesium halides, dialkoxymagnesiums, alkoxymagnesium halides, magnesium oxyhalides, dialkylmagnesiums, magnesium oxide, magnesium hydroxide, and carboxylates of magnesium.

1. The purpose of this document is to provide information regarding the status of the project. The project is currently in the planning stage and is expected to be completed by the end of the year. The project is being managed by the Project Manager, who is responsible for ensuring that the project is completed on time and within budget. The project is being funded by the Department of Defense, and the results of the project will be used to improve the security of the United States.

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8. The project is being managed by the Project Manager, who is responsible for ensuring that the project is completed on time and within budget. The project is being funded by the Department of Defense, and the results of the project will be used to improve the security of the United States.

EXAMPLE 1

7.7 mmoles of a 5:1 molar mixture of triethylaluminum (TEAL) and triisobutylaluminum (TIBAL) in 7.7 ml hexane/heptane mixture (1:3 volume ratio) were placed in a stainless steel bomb along with 0.05 mmole of cyclohexylmethyldimethoxysilane (CMDS) and mixed by shaking. A mineral oil slurry of 30 mg of a conventional supported Ziegler-Natta catalyst component was introduced into the transfer bomb followed by a mineral oil slurry of 33 mg of diphenylmethyl (fluorenyl)(cyclopentadienyl)zirconium dichloride supported on MAO-treated silica prepared as described above. The contents of the transfer bomb were mixed and charged along with 750 g of propylene into a 2 liter Zipperclave reactor containing 750 g of propylene and 32 mmoles hydrogen. The reactor mixture was stirred at room temperature for 7 minutes and the temperature was increased to 60°C. The polymerization continued for one hour at 60°C. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer analysis is shown in Table 1.

Molecular weight distribution (MWD) is the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n): $MWD = M_w/M_n$. This ratio is also known as polydispersity.

Xylene solubles are measured by dissolving the polymer in hot xylene, cooling the solution to 0°C and precipitating out the isotactic form. The xylene solubles are the wt% of the polymer that was soluble in the cold xylene.

The percent SPP was determined by NMR analysis.

EXAMPLE 2

The procedures of Example 1 were repeated except that 69 mg of the supported metallocene catalyst, 9.4 mmole of the TIBAL/TEAL mixture and 0.065 mmole of CMDS were used. The polymer analysis is shown in Table I.

EXAMPLE 3

The procedures of Example 1 were repeated except that 133 mg of the supported metallocene catalyst, 12.8 mmole of the TIBAL/TEAL mixture and 0.086 mmole of CMDS were used. The polymer analysis is shown in Table I.

EXAMPLE 4

The procedures of Example 1 were repeated except that 266 mg of the supported metallocene catalyst, 18.7 mmole TIBAL/TEAL mixture and 0.125 mmole of CMDS were used. The polymer analysis is shown in Table I.

COMPARATIVE EXAMPLE 1

The procedures of Example 1 were repeated except that only the conventional Ziegler-Natta (isospecific) catalyst was present. The polymer analysis is shown in Table I.

COMPARATIVE EXAMPLE 2

The procedures of Example 1 were repeated except that only the supported metallocene (syndiospecific) catalyst was present. The polymer analysis is shown in Table I.

TABLE I

EXAMPLE	%sPP	MWD (M_w/M_n)	Melt Flow Index (g/10 min)	Xylene Solubles (%)
1	<2	9.0	2.9	3.6
2	2.34	9.6	4.0	4.6
3	4.0	8.2	3.5	3.9
4	13.9	8.3	4.7	5.4
Comp.Ex 1	100	2.4	3.5	3.2
Comp.Ex 2	0%	8.4	2.1	2.4

TO ALL WHOM THESE PRESENTS SHALL COME, I, JAMES M. SMITH, of the County of [] State of [], do hereby certify that the within and foregoing is a true and correct copy of the original of the same, as the same appears from the records of the [] of the County of [] State of [], and that the same is a true and correct copy of the original of the same, as the same appears from the records of the [] of the County of [] State of [].

IN WITNESS WHEREOF, I have hereunto set my hand and the seal of the County of [] State of [], this [] day of [] A.D. 19[].

JAMES M. SMITH, [] of the County of [] State of [].

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2. The polymer blend of Claim 1 wherein the syndiotactic polypropylene is less than about 2% by weight.

3. A process for obtaining a reactor polymer blend comprising:

5 a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound as given by a Ti:Zr molar ratio ranging up to about 0.48:1;

10 b) introducing propylene to the reaction zone;

c) maintaining the reaction zone at polymerization conditions;

d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

15 wherein the syndiotactic polypropylene is up to about 4% by weight and wherein the molecular weight distribution is above about 7.4.

4. The process of Claim 3 wherein the syndiotactic polypropylene is less than about 2% by weight.

5. A biaxially oriented film comprising a reactor polymer blend of:

20 a) isotactic polypropylene;

b) syndiotactic polypropylene;

wherein the syndiotactic polypropylene is up to about 13.9% by weight and

25 wherein the percent haze of the film is less than about 5%.

6. The biaxially oriented film of Claim 5 wherein the syndiotactic polypropylene is about 2.34% to about 13.9% by weight.

30 7. The biaxially oriented film of Claim 5 wherein the percent haze is from about 3% to about 5%.

8. A process for obtaining a reactor polymer blend comprising:

35 a) allowing a conventional Ziegler-Natta catalyst component, a metallocene compound supported on silica treated with an alumoxane and an organoaluminum compound to contact each other to form activated catalysts in a reaction zone

wherein the ratio of the conventional Ziegler-Natta catalyst component to metallocene compound as given by a Ti:Zr molar ratio up to about 0.21:1.

40 b) introducing propylene to the reaction zone;

c) maintaining the reaction zone at polymerization conditions;

d) withdrawing a polymer blend of isotactic polypropylene and syndiotactic polypropylene

wherein the syndiotactic polypropylene is up to about 13.9% by weight and

e) making a biaxially oriented film

45 wherein the percent haze of the film is less than about 5%.

9. The process of Claim 8 wherein the syndiotactic polypropylene is from about 2.34 to about 13.9% by weight.

10. The process of Claim 8 wherein the percent haze is from about 3% to about 5%.

50 11. A polymer blend comprising a reactor blend of:

a) isotactic polypropylene;

55 b) syndiotactic polypropylene; wherein the syndiotactic polypropylene is within a range from about 2.34% by weight to about 13.9% by weight and

wherein the melt flow is above about 3.5 g/10".

12. The polymer blend of Claim 11 wherein the melt flow is from about 3.5 g/10 min to about 4.7 g/10 min.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 10 9107

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 536 104 (FINA TECHNOLOGY) 7 April 1993 * page 3, line 19 - page 4, line 34 * ---	1-16	C08L23/00 C08L23/10
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 95-237198 XP002014138 & JP-A-07 145 202 (MITSUI TOATSU) , 6 June 1995 * abstract * -----	1-16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08J C08L C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 September 1996	Examiner Schmidt, H
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